

## Claims

1. A polymer film based on polyazoles which is obtainable by a process comprising the steps

- A) mixing of one or more aromatic tetraamino compounds with one or more aromatic carboxylic acids or esters thereof which contain at least two acid groups per carboxylic acid monomer, or mixing of one or more aromatic and/or heteroaromatic diaminocarboxylic acids, in polyphosphoric acid to form a solution and/or dispersion,
- B) application of a layer using the mixture from step A) to a support,
- C) heating of the sheet-like structure/layer obtainable according to step B) under inert gas at temperatures of up to 350°C, preferably up to 280°C, to form the polyazole polymer,
- D) treatment of the polymer film formed in step C) (until it is self-supporting),
- E) detachment of the polymer film formed in step D) from the support,
- F) removal of the polyphosphoric acid or phosphoric acid present and drying.

2. The polymer film as claimed in claim 1, characterized in that aromatic tetraamino compounds used are 3,3',4,4'-tetraaminobiphenyl, 2,3,5,6-tetraaminopyridine, 1,2,4,5-tetraaminobenzene, bis(3,4-diaminophenyl) sulfone, bis(3,4-diaminophenyl) ether, 3,3',4,4'-tetraaminobenzophenone, 3,3',4,4'-tetraaminodiphenylmethane and 3,3',4,4'-tetraaminodiphenyl-dimethylmethane.

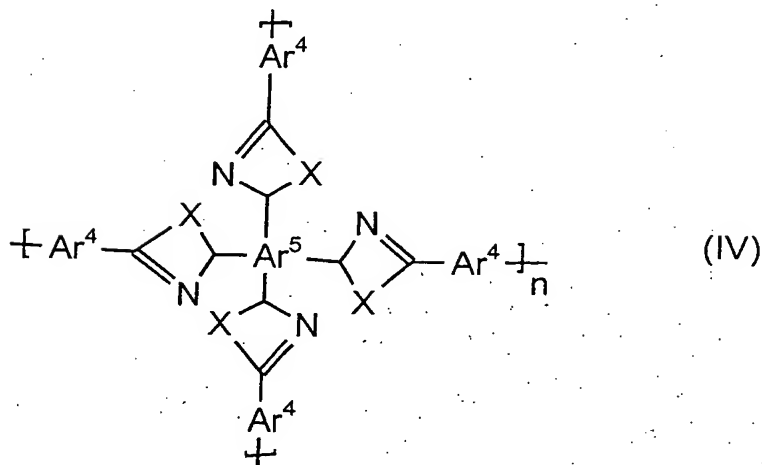
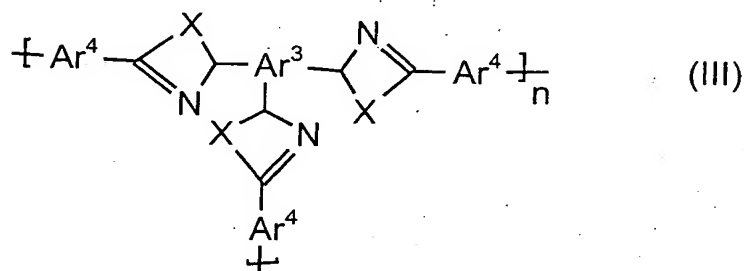
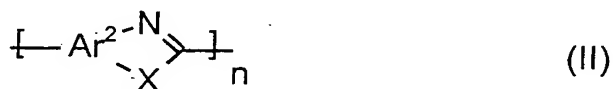
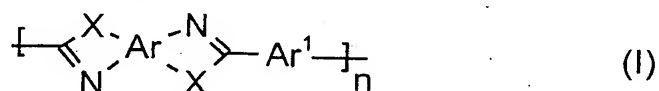
3. The polymer film as claimed in claim 1, characterized in that aromatic dicarboxylic acids used are isophthalic acid, terephthalic acid, phthalic acid, 5-hydroxyisophthalic acid, 4-hydroxyisophthalic acid, 2-hydroxyterephthalic acid, 5-aminoisophthalic acid, 5-N,N-dimethylaminoisophthalic acid, 5-N,N-diethylaminoisophthalic acid, 2,5-dihydroxyterephthalic acid, 2,5-dihydroxyisophthalic acid, 2,3-dihydroxyisophthalic acid, 2,3-dihydroxyphthalic acid, 2,4-dihydroxyphthalic acid, 3,4-dihydroxyphthalic acid, 3-fluorophthalic acid, 5-fluoroisophthalic acid, 2-fluoroterephthalic acid, tetrafluorophthalic acid, tetrafluoroisophthalic acid, tetrafluoroterephthalic acid, 1,4-naphthalene-dicarboxylic acid, 1,5-naphthalenedicarboxylic acid, 2,6-naphthalenedicarboxylic acid, 2,7-naphthalenedicarboxylic acid, diphenic acid, 1,8-dihydroxynaphthalene-3,6-dicarboxylic acid, bis(4-carboxyphenyl) ether, benzophenone-4,4'-dicarboxylic acid, bis(4-carboxyphenyl) sulfone, biphenyl-

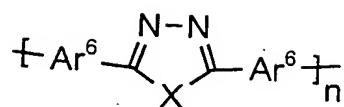
4,4'-dicarboxylic acid, 4-trifluoromethylphthalic acid, 2,2-bis(4-carboxyphenyl)-hexafluoropropane, 4,4'-stilbenedicarboxylic acid, 4-carboxycinnamic acid, or their C1-C20-alkyl esters or C5-C12-aryl esters, or their acid anhydrides or acid chlorides.

4. The polymer film as claimed in claim 1, characterized in that aromatic carboxylic acids used are tricarboxylic acids, tetracarboxylic acids or their C1-C20-alkyl esters or C5-C12-aryl esters or their acid anhydrides or their acid chlorides, preferably 1,3,5-benzenetricarboxylic acid (trimesic acid); 1,2,4-benzenetricarboxylic acid (trimellitic acid); (2-carboxyphenyl)imino-diacetic acid; 3,5,3'-biphenyltricarboxylic acid; 3,5,4'-biphenyltricarboxylic acid and/or 2,4,6-pyridinetricarboxylic acid.
5. The polymer film as claimed in claim 1, characterized in that aromatic carboxylic acids used are tetracarboxylic acids, their C1-C20-alkyl esters or C5-C12-aryl esters or their acid anhydrides or their acid chlorides, preferably benzene-1,2,4,5-tetracarboxylic acid, naphthalene-1,4,5,8-tetracarboxylic acid, 3,5,3',5'-biphenyltetracarboxylic acid; benzophenonetetracarboxylic acid, 3,3',4,4'-biphenyltetracarboxylic acid, 2,2',3,3'-biphenyltetracarboxylic acid, 1,2,5,6-naphthalenetetracarboxylic acid, 1,4,5,8-naphthalenetetracarboxylic acid.
6. The polymer film as claimed in claim 4, characterized in that the content of tricarboxylic acids and tetracarboxylic acids (based on dicarboxylic acid used) is from 0 to 30 mol%, preferably from 0.1 to 20 mol%, in particular from 0.5 to 10 mol%.
7. The polymer film as claimed in claim 1, characterized in that heteroaromatic carboxylic acids used are heteroaromatic dicarboxylic acids and tricarboxylic acids and tetracarboxylic acids in which at least one nitrogen, oxygen, sulfur or phosphorus atom is present in the aromatic, preferably pyridine-2,5-dicarboxylic acid, pyridine-3,5-dicarboxylic acid, pyridine-2,6-dicarboxylic acid, pyridine-2,4-dicarboxylic acid, 4-phenyl-2,5-pyridinedicarboxylic acid, 3,5-pyrazoledicarboxylic acid, 2,6-pyrimidinedicarboxylic acid, 2,5-pyrazine-dicarboxylic acid, 2,4,6-pyridinetricarboxylic acid, benzimidazole-5,6-dicarboxylic acid and also their C1-C20-alkyl esters or C5-C12-aryl esters or their acid anhydrides or their acid chlorides.
8. The polymer film as claimed in claim 1, characterized in that a polyphosphoric

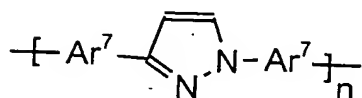
acid having an assay calculated as  $P_2O_5$  (acidimetric) of at least 83% is used in step A).

9. The polymer film as claimed in claim 1, characterized in that a solution or a dispersion/suspension is produced in step A).
10. The polymer film as claimed in claim 1, characterized in that a polyazole-based polymer comprising recurring azole units of the general formula (I) and/or (II) and/or (III) and/or (IV) and/or (V) and/or (VI) and/or (VII) and/or (VIII) and/or (IX) and/or (X) and/or (XI) and/or (XII) and/or (XIII) and/or (XIV) and/or (XV) and/or (XVI) and/or (XVII) and/or (XVIII) and/or (XIX) and/or (XX) and/or (XXI) and/or (XXII)

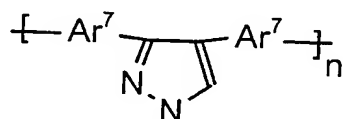




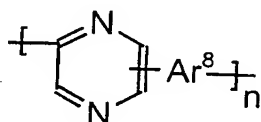
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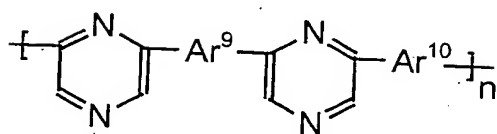
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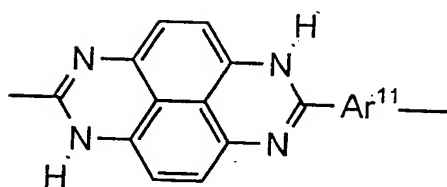
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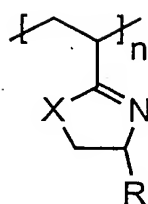
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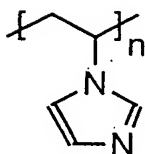
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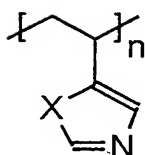
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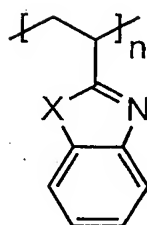
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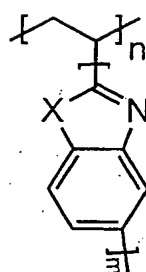
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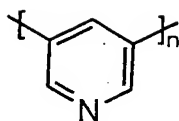
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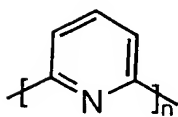
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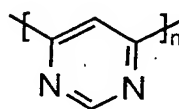
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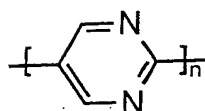
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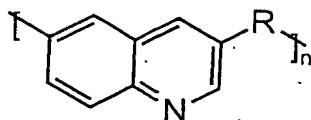
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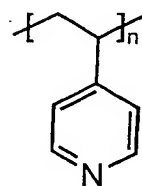
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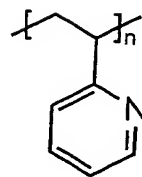
(XIX)



(XX)



(XXI)



(XXII)

where

the radicals Ar

are identical or different and are each a tetravalent aromatic or heteroaromatic group which can be monocyclic or polycyclic,

5 the radicals Ar<sup>1</sup>

are identical or different and are each a divalent aromatic or heteroaromatic group which can be monocyclic or polycyclic,

the radicals Ar<sup>2</sup>

are identical or different and are each a divalent or trivalent aromatic or heteroaromatic group which can be monocyclic or polycyclic,

10 the radicals Ar<sup>3</sup>

are identical or different and are each a trivalent aromatic or heteroaromatic group which can be monocyclic or polycyclic,

the radicals Ar<sup>4</sup>

are identical or different and are each a trivalent aromatic or heteroaromatic group which can be monocyclic or polycyclic,

15 the radicals Ar<sup>5</sup>

are identical or different and are each a tetravalent aromatic or heteroaromatic group which can be monocyclic or polycyclic,

20 the radicals Ar<sup>6</sup>

are identical or different and are each a divalent aromatic or heteroaromatic group which can be monocyclic or polycyclic,

the radicals Ar<sup>7</sup>

are identical or different and are each a divalent aromatic or heteroaromatic group which can be monocyclic or polycyclic,

25 the radicals Ar<sup>8</sup>

are identical or different and are each a trivalent aromatic or heteroaromatic group which can be monocyclic or polycyclic,

the radicals Ar<sup>9</sup>

are identical or different and are each a divalent or trivalent or tetravalent aromatic or heteroaromatic group which can be monocyclic or polycyclic,

30 the radicals Ar<sup>10</sup>

are identical or different and are each a divalent or trivalent aromatic or heteroaromatic group which can be monocyclic or polycyclic,

35 the radicals Ar<sup>11</sup>

are identical or different and are each a divalent aromatic or heteroaromatic group which can be monocyclic or polycyclic,

the radicals X

are identical or different and are each oxygen, sulfur or an amino group which bears a hydrogen atom, a group

having 1-20 carbon atoms, preferably a branched or unbranched alkyl or alkoxy group, or an aryl group as further radical,

the radicals R

are identical or different and are each hydrogen, an alkyl group or an aromatic group, with the proviso that R in the formula (XX) is not hydrogen, and

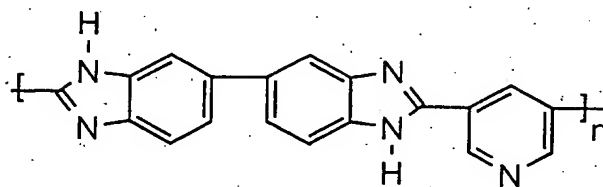
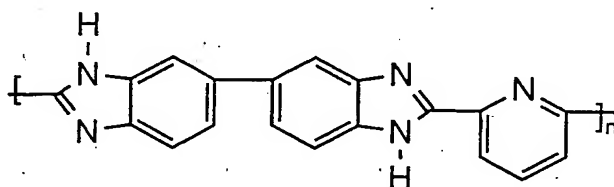
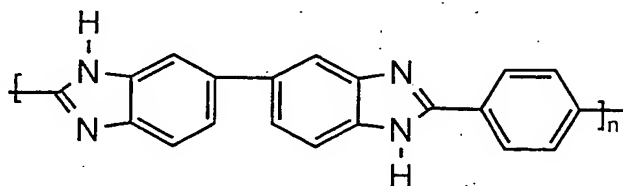
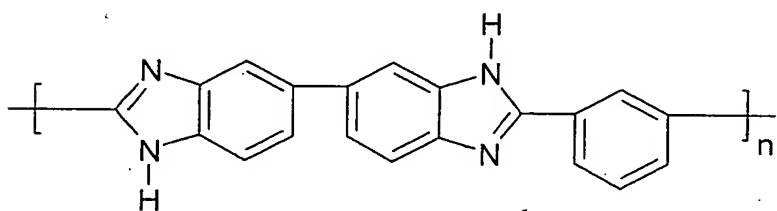
 $n, m$ 

are each an integer greater than or equal to 10, preferably greater than or equal to 100,

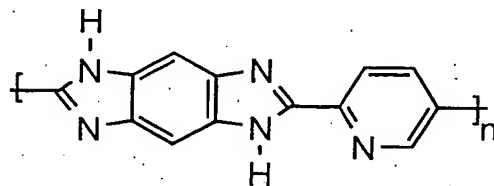
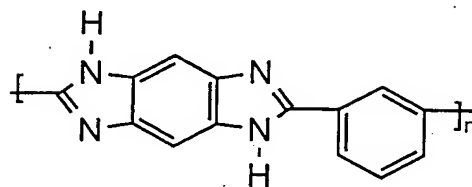
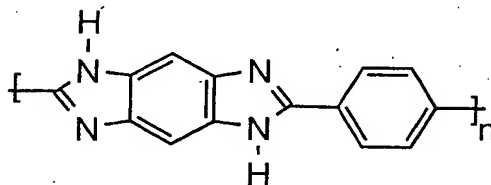
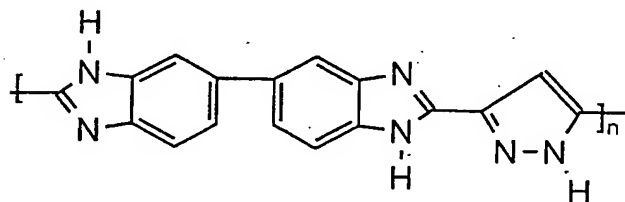
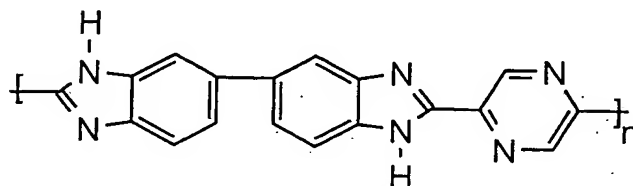
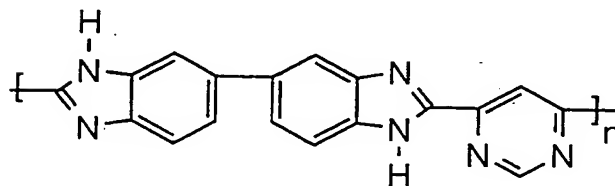
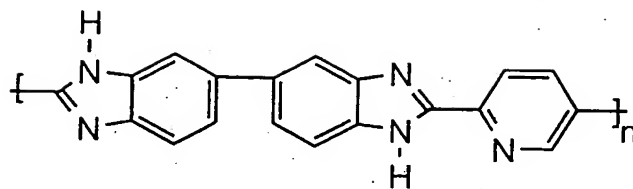
is formed in step C).

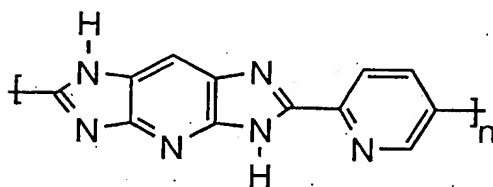
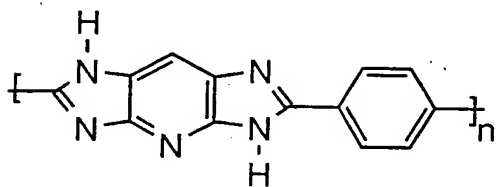
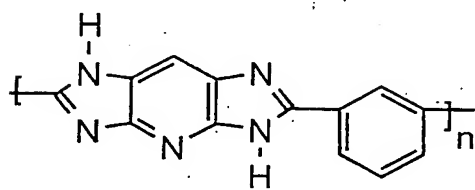
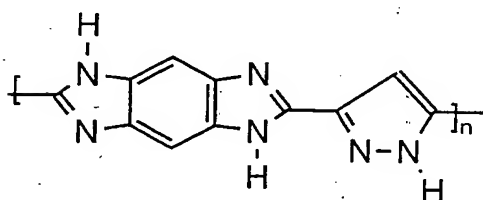
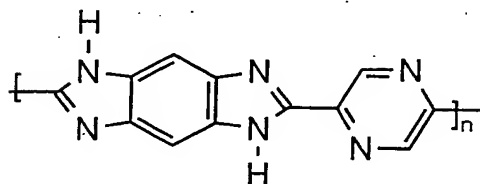
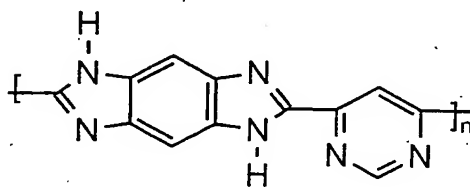
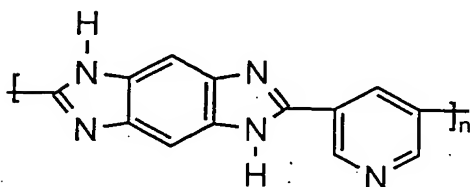
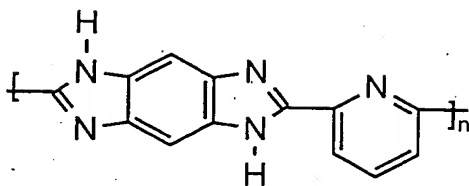
11. The polymer film as claimed in claim 1, characterized in that a polymer selected from the group consisting of polybenzimidazole, poly(pyridines), poly(pyrimidines), polyimidazoles, polybenzothiazoles, polybenzoxazoles, polyoxadiazoles, polyquinoxalines, polythiadiazoles and poly(tetrazapyrenes) is formed in step C).

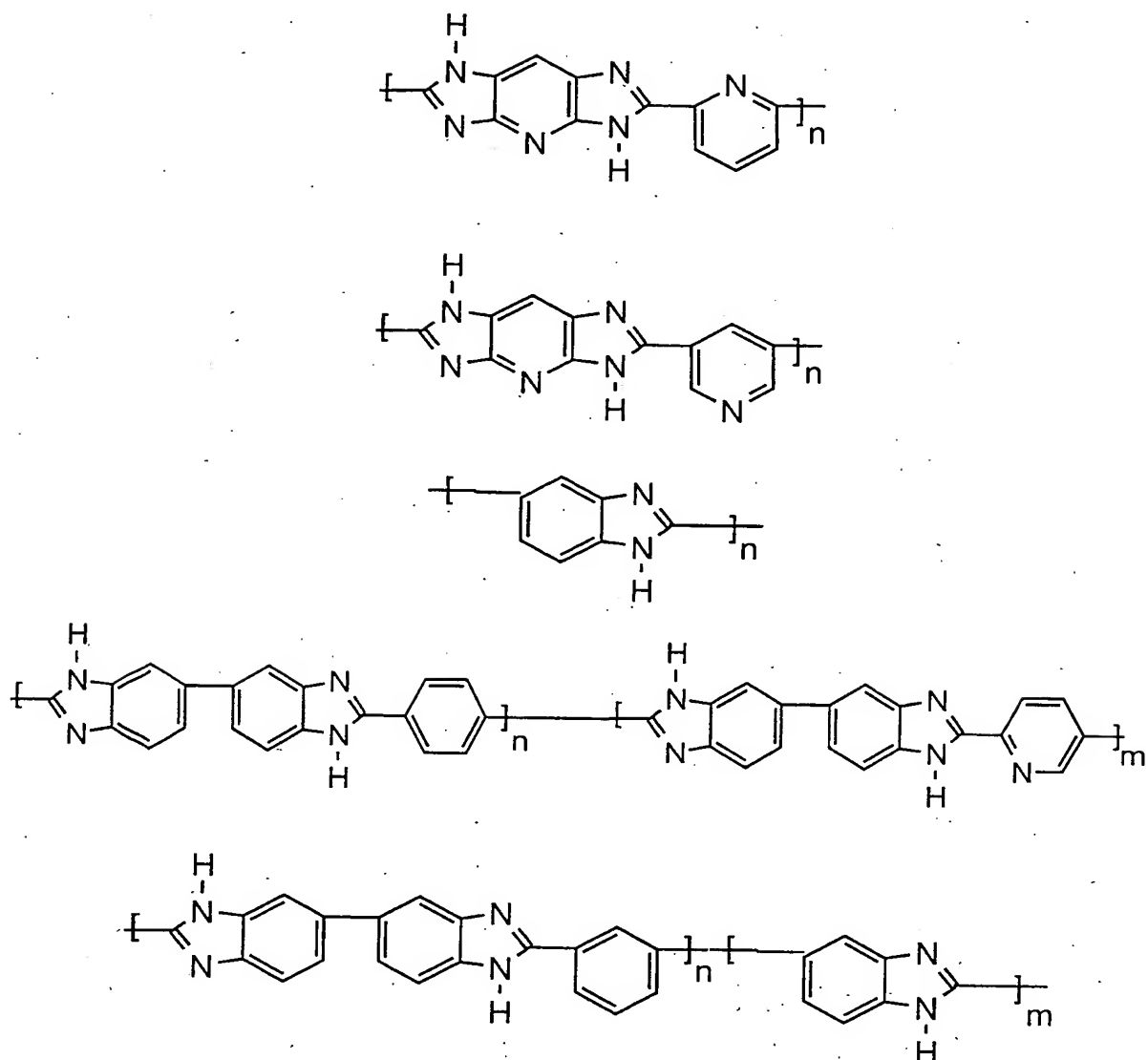
12. The polymer film as claimed in claim 1, characterized in that a polymer comprising recurring benzimidazole units of the formula











where n and m are each an integer greater than or equal to 10, preferably greater than or equal to 100, is formed in step C).

13. The polymer film as claimed in claim 1, characterized in that the viscosity is adjusted by addition of phosphoric acid after step A) and before step B).
14. The polymer film as claimed in claim 1, characterized in that the membrane produced according to step C) is treated in the presence of moisture at temperatures and for a time sufficient for the membrane to be self-supporting and to be able to detached from the support without damage.
15. The polymer film as claimed in claim 1, characterized in that the treatment of the membrane in step D) is carried out at temperatures of from  $>0^{\circ}\text{C}$  to

150°C, preferably at temperatures in the range from 10°C to 120°C, in particular from room temperature (20°C) to 90°C, in the presence of moisture or water and/or water vapor.

- 5 16. The polymer film as claimed in claim 1, characterized in that the treatment of the membrane in step D) is carried out for from 10 seconds to 300 hours, preferably from 1 minute to 200 hours.
- 10 17. The polymer film as claimed in claim 1, characterized in that the removal of the polyphosphoric acid or the phosphoric acid in step F) is carried out by means of a treatment liquid.
- 15 18. The polymer film as claimed in claim 1, characterized in that the treatment in step D) is omitted.
19. The polymer film as claimed in claim 1, characterized in that the polymer film is not self-supporting after the treatment in step D) and remains on the support for further processing.
- 20 20. The use of the polymer film as claimed in any of claims 1 to 19 as filter medium in gas filtration, as membrane in the field of gas separation and/or gas purification, in reverse osmosis, nanofiltration, ultrafiltration, microfiltration, dialysis, electrodialysis, as substrate for electric circuits, as battery separators, as membranes in electrolysis, as protective film for electric cables, as insulator in electrical components and devices such as capacitors, as protective film for metal and other surfaces.
- 25 21. A polymer based on polyazoles as defined in any of claims 10 to 12 whose molecular weight expressed as intrinsic viscosity is at least 1.4 dl/g and which is obtainable by a process comprising the steps
- 30 A) mixing of one or more aromatic tetraamino compounds with one or more aromatic carboxylic acids or esters thereof which contain at least two acid groups per carboxylic acid monomer, or mixing of one or more aromatic and/or heteroaromatic diaminocarboxylic acids, in polyphosphoric acid to form a solution and/or dispersion,
- 35 B) heating of the mixture obtainable according to step A) under inert gas at temperatures of up to 350°C, preferably up to 280°C, to form the polyazole polymer,
- C) precipitation of the polymer formed in step B), isolation and drying of

the polymer powder obtained.

- 5 22. A polymer fiber based on polyazoles as defined in any of claims 10 to 12 whose molecular weight expressed as intrinsic viscosity is at least 1.4 dl/g and which is obtainable by a process comprising the steps
- 10 A) mixing of one or more aromatic tetraamino compounds with one or more aromatic carboxylic acids or esters thereof which contain at least two acid groups per carboxylic acid monomer, or mixing of one or more aromatic and/or heteroaromatic diaminocarboxylic acids, in polyphosphoric acid to form a solution and/or dispersion,
  - B) heating of the mixture from step A) at temperatures of up to 350°C, preferably up to 280°C, to form the polyazole polymer,
  - C) extrusion of the polyazole polymer formed in step B) to form fibers,
  - 15 D) introduction of the fibers formed in step C) into a bath of liquid,
  - E) isolation and drying of the fibers obtained.
23. The polymer fiber as claimed in claim 22, characterized in that the fibers formed in step C) are introduced into a precipitation bath.
- 20 24. The polymer fiber as claimed in claim 22, characterized in that the polyazole polymer extruded in step C) is saturated with a gas, preferably in the supercritical state, so that the gas forms pores on subsequent expansion.